Treatment of Aqueous Solutions of Lipophilic Cationic Dye Using Activated Carbon and Ferrous Oxide Synthesized Nanoparticles

Ahmed Qasim Ubaid[1*], Nadia Mohammed Majeed[2], Ahmed Mohammed Ali Savore[3], Mohammed Jawad Salih Al-Haidarey[4]

Abstract

Adsorption is one of the promising strategies for aqueous dye remediation. A lot of attention has been paid to textile wastewater treatment using smart materials. In this study, we formed the N-FeO to test its properties by using FTIR and TEM technique. We also tested AC, N-FeO and mixed N-FeO/AC to investigate the adsorption efficiency of lipophilic cationic dye (LCD) removal from aqueous solutions of each individually under. The results showed that the removal percentage of lipophilic cationic dye by using activated crbon was increasing significantly with AC wight (P-value < 0.01), and the highst removal was to 0.1 ppm of dye (52%). While the lowest dye removal percentage was 14.3% of 1ppm dye concentration and 0.05g AC. The rmoval of dye, by using N-FeO, was depant on the concentration of dye and the amount of N-FeO. The highst percentage of dye removal was 45% ±3.69 of 0.1 ppm concentration with using 0.3g and 0.35 g of N-FeO. While the lowest removal percentage of dye was 7.3%±2.49 of 1ppm with using 0.05g of N-FeO. The using of N-FeO/AC mixture leads to a significant removal percentage of dye in different concentrations compared with using each of them a lone. By this mixture, the highest removal of dye reached to 98%±3.47, 92%±3.96, and 88%±1.44 of 0.1ppm, 0.5ppm, and 1ppm respectively by using 0.35g of N-FeO/AC mixture. While the lowest dye removal percentage was 54%±1.1, 46%±0.98, and 40%±2.49 of 0.1ppm, 0.5ppm, and 1ppm respectively by using 0.05g of N-FeO/AC mixture. This study suggested that the increase in adsorption at low dye concentration was due to the availability of active sites that were saturated While the adsorbing surface area will increase with the N-FeO/AC mixture, the percentage of dye removal at constant temperature will also increase, and it is nessesary to using more chemometric test of this mixture for testing the best removal environment of this kind of dye.

Key Words: N-FeO, Lipophilic Cationic Dye, Activated Carbon.

DOI Number: 10.14704/nq.2021.19.6.NQ21066 **NeuroQuantology 2021; 19(6):41-47**

Introduction

Nanotechnology has the ability to replace traditional methods and improve wastewater technologies for the next generation (Ajmal *et al*., 2019; Bibi *et al*., 2019). Nanoparticles are used for the treatment and purification of wastewater due to their properties such as high reactivity, high surface area, nctionalization and efficiency (Fu adsorption is widely considered to be a very efficient because of the relatively low cost, increased efficiency and effectiveness (Jamil *et al*., 2019; Bhatti *et al*., 2018). Petrochemical, paper, textile and food industries, along with other industrial enterprises, produce a wide range of wastes. Industrial wastewater, such as dissolved organic matter and colloidal suspension, are the main components of these industrial effluents. Effluents with different compositions require different treatment.

Corresponding author: Ahmed Qasim Ubaid
Address: [1*]College of Education for Pure Sciences, Wasit University, Iraq; [2]Department of Basic Science, College of Dentistry, Wasit University, Iraq; [3]Education Directorate of Wasit Province, Iraq; [4]Department of Ecological Sciences, University of Kufa-Iraq.
[1*]E-mail: aubaid@uowasit.edu.iq

Received: 25 March 2021 **Accepted:** 12 May 2021

Coagulation and flocculation, bed filtration, membrane filtration, precipitation, biodegradation and oxidation cannot be effectively treated with that industrial wastewater (Minas *et al*., 2017; Jafarinejad, 2017). Adsorption techniques have significant advantages, such as adaptability, ease of use, and reliability (Hamilton-Amachree and Iroha, 2020; Jonidi Jafari *et al*., 2016). Adsorption has emerged as a useful technique for the maintenance of waste. Many different methods have been applied in water treatment such as filtration, precipitation, adsorption, filtration using chlorine or hydrogen peroxide, bacteria and membrane systems. To date, some maghemite supported on cross-linked chitosan, mesoporous biochars, silica-coated magnetite spheres, activated carbon and clays are applied as adsorbents (Kakavandi et al., 2018; Babaei et al., 2016). Recently, the adsorption of dyes and metal oxide was strongly concentrated on nanoparticles (NPs). Due to its porous structures and wide surface areas, NPs have provided promising efficiency (Kakavandi et al., 2019). Other studies have also shown that the self-composite nanostructures have been prepared using different moieties and used in different fields, for example, nanocomposites that use different types of compounds as catalysts (He et al., 2019), nanostructures of palladium with dyes to create a visible signature that could replace ink (Wang et al., 2019), and composite materials with two types of components that can be used in different mechanisms, such as a gas sensor (Hou et al., 2019) and a catalyst (Zhu et al., 2019). The lipophilic cationic dye (safranin) is one of the oldest dyes are used. $C_{20}H_{19}N_4Cl$ is the molecular formula for this dye (Bhateria and Singh, 2019). It is water soluble (Ciambell et al., 2019), so it used in food and dessert coloring by several industries (e.g. paper, textile and silk industries), despite the advantages of this dye, but it causes water pollution when discharged into the water and affects human health (Sayhood and Mohammed, 2015). There are several methods of removing dyes from water and one of the most relevant technologies is adsorption. Adsorption technology is used because it is easy to use, inexpensive and highly effective to absorb dyes from water (Sahoo and Prelot, 2020). Recently, adsorbent activated carbon by adsorption technology has been commonly used in the processes of removal. Activated carbon has a wide surface area and quantity that can ideally be used to eliminate dyes as an adsorption (Aljafery et al., 2018). Due to its good qualities, which are highly effective, inexpensive and abundant, the use of nano-iron oxide has started to extract dyes from water in the last few years, and nano-iron oxide is used in many applications, including medicine and chemistry, industrial water treatment and other applications (Kaur et al., 2015).

From the above aforementioned facts, Activated carbon (AC), FeO nanoparticles (N-FeO), and mixture of N-FeO/AC efficacies were evaluated for the absorption of lipophilic cationic dye.

Material and Methods

Preparation of N-FeO: Using a precipitation process, FeO nanoparticles were synthesized. By dissolving FeSO4 in deionized water through a conical flask connected to the solution of nitrogen purging. Then, a well-mixed prepared iron solution was applied drop-wise to the NaOH solution. The final pH of the iron solution was held at 10. After that, for two hours, the temperature was increased to 80°C. The salts were separated by magnetic separation from the precipitated nanoparticles and rinsed with deionized water 5 times until the pH of the supernatant was reduced to 8.5 ranges. The intensely greenish precipitated nanoparticles were dried for two hours in an oven at 70 °C (Girginova *et al*., 2010). FTIR (SHIMADZU IR Tracer-100-MIRacle 10) analysis confirmed the formation of γ-Fe2O3 from Fe3O4 at calcination at 300∘C. Morphology and particle size were examined by High resolution transmission electron microscopy (JEM-2100F, JEOL) by diluted of a few drops of nanocomposite solution into 1 ml of ethanol, then placed onto a carbon coated copper grid and allowed to evaporate (Kostyukova and Chung, 2016).

Determine the λ_{max} of lipophilic cationic dye: UV-visible spectrometer (UV-1900i UV-VIS Spectrophotometer from Shimadzu) within the range of 200-800 nm with a quartz cell (1cm) were used to determine the maximum wavelength of this dye. Triplicates of five gradient concentrations (0.5, 1, 2, 5 and 10 mg/L) were prepared from lipophilic cationic dye (LCD) to set the calibration curve, and then the absorption of these concentrations was determined at the maximum dye wavelength, and then the calibration curve was formed between the absorption and the concentration. The Least Squares approach has been used as a method for statistically treating absorption values (Fig. 1). We found that the λ_{max} for LCD is 560nm.

Determination of potential dye adsorption: Three LCD concentrations (0.1, 0.5, and 1 mg/L) were taken in 100 ml of distilled water to test our hypothesis. To determine the removal efficiency of LCD by AC and N-FeO, the equivalent percentage of activated carbon and N-FeO were combined in six different weights (0.05, 0.1, 0.2, 0.25, 0.3, 0.35 gm) then comparion the removal effeciancy with using each of AC and N-FeO separately in the same weights. For each test, with continuous solution stirring, the 100 ml solution was triplicat applied separately for 20 minutes, respectively. By using filter paper (Whatman #1) filtered the solution, then we measured the remaining filter's absorbance.

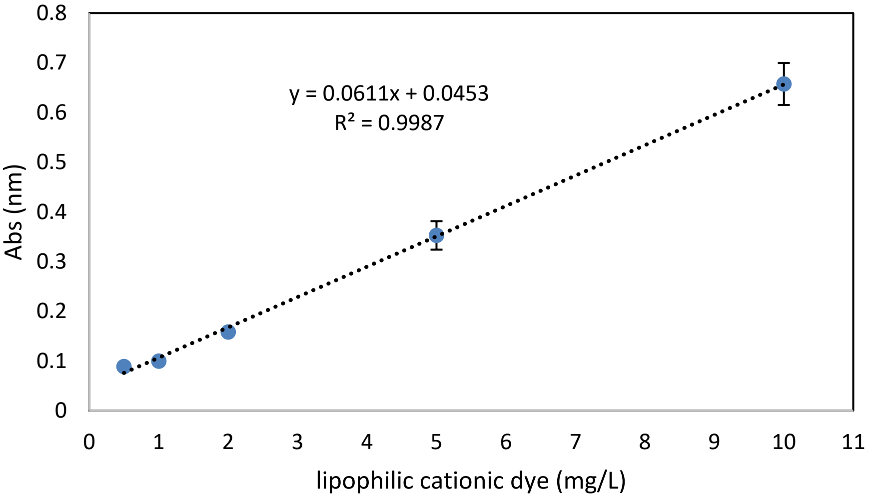

Fig. 1. Calibration curve for lipophilic cationic dye (mg/L)

Result and Discussion

Characters of synthesized N-FeO: Fig. 2 showed that the IR absorption bands were about 443, 590, and 639 and that were due to the vibrations of Fe–O bonds in magnetite and these absorption findings were similar to some previous studies.

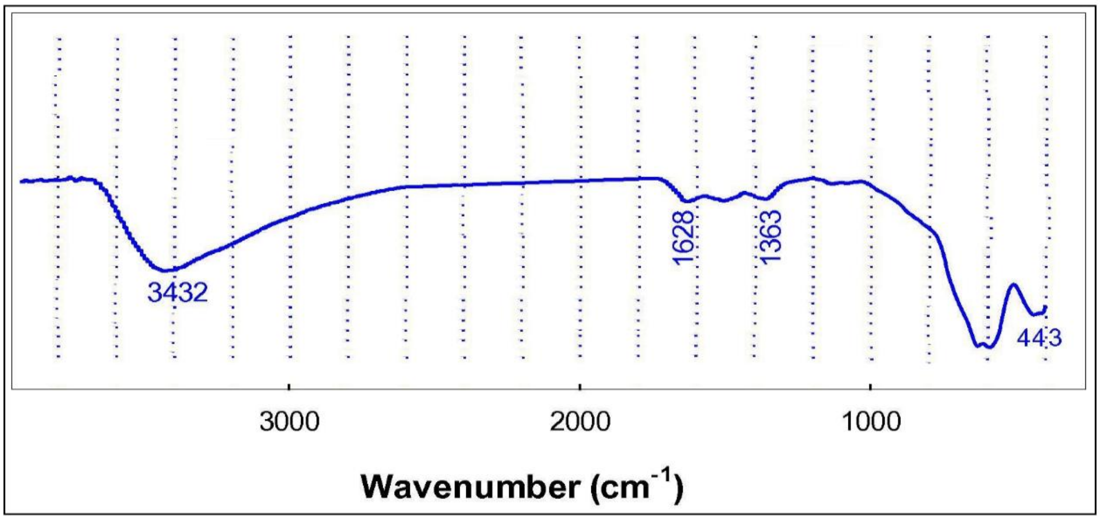

Fig. 2. The FTIR spectra of FeO nanoparticles

The morphology of particles prepared under various molar ratios of iron oxide nanoparticles has been studied. The TEM picture showed that, as shown in Fig.3, the N-FeO appeared as hexagonal sheets, square sheets, irregular shaped, multiple twins, octahedral, and cubic. The hexagonal sheet was semi-transparent, the mean diameters were around 200±38nm. The current results were agreed with Mazruaa *et al.* (2019).

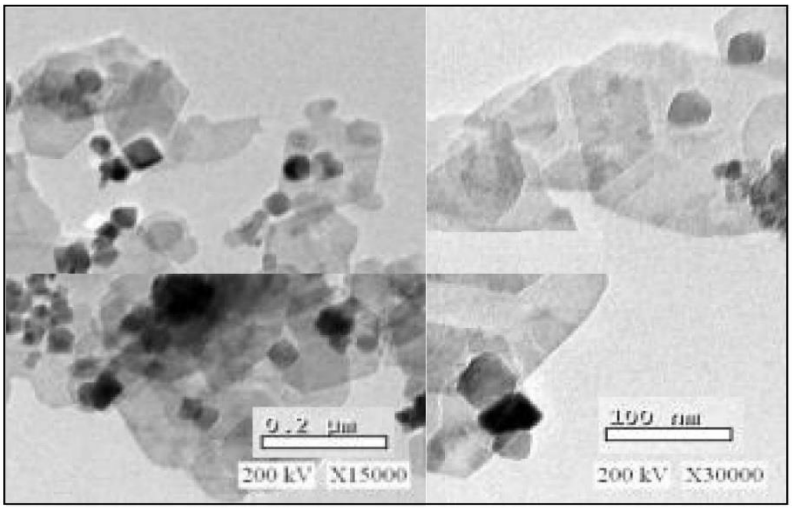

Fig. 3. TEM photographs of FeO nanoparticles

Using AC to dye removal: The most common adsorbent for the removal of many organic pollutants is activated carbon (Yu *et al*., 2017). Activated carbon have wide surface area and abundance which preferable to use as a sorbent to remove dyes (Aljafery *et al*., 2018). As showen in Fig. 4, the removal percentage of lipophilic cationic dye by using activated crbon was increasing significantly with AC wight (P-value < 0.01), and the highst removal was to 0.1 ppm of dye (52%). While the lowest dye removal percentage was 14.3% of 1ppm dye concentration and 0.05g AC. This result was agree with Dahlan *et al*. (2014) and Yu *et al*. (2017). The dye molecules will combine with the activated carbon surface until that surface is saturated, meaning that high dye concentrations need more activated carbon surface area to increase the adsorption efficiency technique. Due to its low adsorption power, which is due to limited specific surface area and poor performance of adsorption selection, as well as limitations of functional groups and electrochemical properties of the surface, we need modification AC to be more efficiency (Kuang *et al*., 2020).

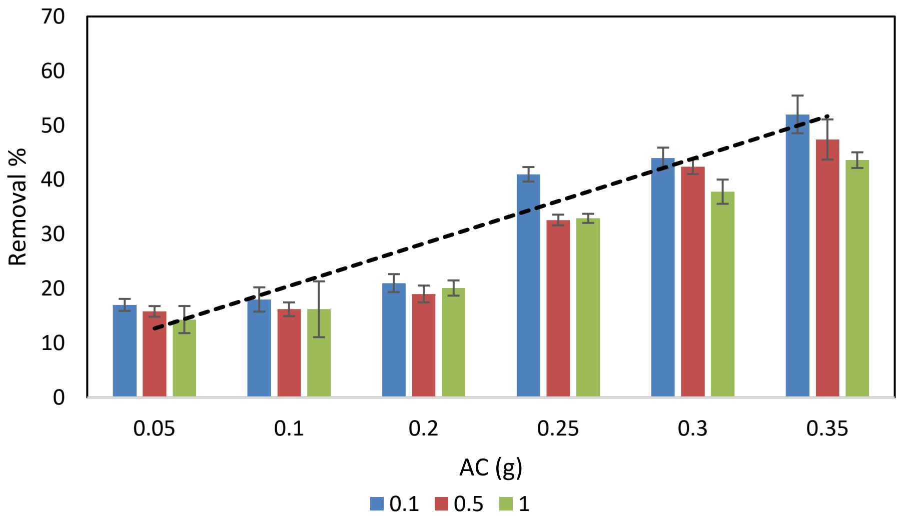

Fig.4. The dye removal percentage by using AC

Using N-FeO to dye removal: As showen in Fig.5, the rmoval of dye was depant on the concentration of dye and the amount of N-FeO. The highst percentage of dye removal was 45% ±3.69 of 0.1 ppm concentration with using 0.3g and 0.35 g of N-FeO. While the lowest removal percentage of dye was 7.3%±2.49 of 1ppm with using 0.05g of N-FeO, this results were closed to that was recorded by Noreen *et al.* (2020a) that the removal of dyes depends on the dose of N-FeO (Ishtiaq *et al.*, 2020), concentration of dyes (Noreen *et al.*, 2019; Mushtaq *et al.*, 2016), pH (Ishtiaq *et al.*, 2020), temperature (Kausar *et al.*, 2018), and contact time that the initial adsorption increases before equilibrium is reached due to the availability of active sites (Shoukat *et al.*, 2017).

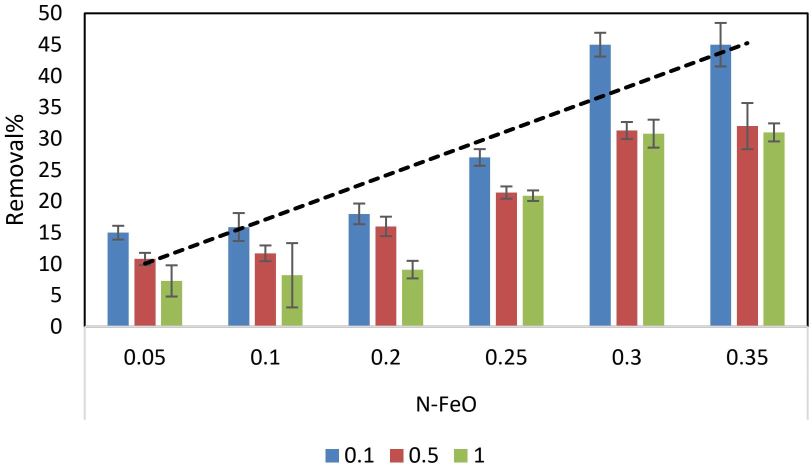

Fig. 5. The dye removal percentage by using N-FeO

Using the combination of AC and N-FeO: The using of N-FeO/AC mixture, in same wight, leads to a significant removal percentage of dye in different concentrations compared with using each of them a lone. By this mixture, the highest removal of dye reached to 98%±3.47, 92%±3.96, and 88%±1.44 of 0.1ppm, 0.5ppm, and 1ppm respectively by using 0.35g of N-FeO/AC mixture. While the lowest dye removal percentage was 54%±1.1, 46%±0.98, and 40%±2.49 of 0.1ppm, 0.5ppm, and 1ppm respectively by using 0.05g of N-FeO/AC mixture. Moreover the removal percentage of dye was gradiant according to the concentration of dye and dose of N-FeO/AC mixture (Fig. 6). This finding is very important to doublicated the removerl percentage and increasing the effeciancy of dye treatment. The increase in adsorption at low dye concentration was due to the availability of active sites that were saturated and the adsorption potential at higher concentration was not significantly increased, thereby increasing the mass transfer force, which overcomes the resistant force responsible for low dye ion adsorption. While the adsorbing surface area will increase with the N-FeO/AC mixture, the percentage of dye removal at constant temperature will also increase (Mushtaq *et al.*, 2016).

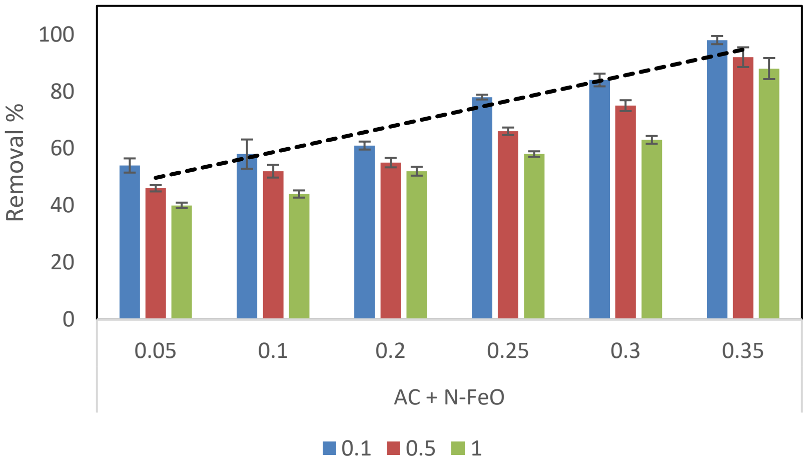

Fig.6. The dye removal percentage by using AC+N-FeO

Conclusion

The created N-FeO appeared as multiple shapes and large adsorbtion area. The using of AC and N-FeO, each a lone, to treatment the LDC leads to remove less than 50% while the use of N-FeO/AC mixture leads to doblicated the removal percentage. So we suggested to using more chemometric test of this mixture for testing the best removal environment of that dye.

Acknowledgement

Authors would like to thank Department of Ecology, University of Kufa for funding this study. Also, would like to thanking Kufa Agency of Scientific Training Services/Iraq for supporting the lab work of this study.

References

Ajmal S, Bibi I, Majid F, Ata S, Kamran K, Jilani K, Iqbal M. Effect of Fe and Bi doping on LaCoO3 structural, magnetic, electric and catalytic properties. *Journal of Materials Research and Technology* 2019; 8(5): 4831-4842.

Aljafery AMA, Sayhood A, Abdulridha WAM, Yousif AM. Evaluation the Tensile Strength of Cold-Cured Acrylic Resin Denture Base Material by Adding Silver Nanoparticles. *Indian Journal of Public Health Research & Development* 2018; 9(10): 917–922.

Mazrouaa AM, Mohamed MG, Fekry M. Physical and magnetic properties of iron oxide nanoparticles with a different molar ratio of ferrous and ferric. *Egyptian Journal of Petroleum* 2019; 28(2): 165-171.

Babaei AA, Alavi SN, Akbarifar M, Ahmadi K, Ramazanpour Esfahani A, Kakavandi B. Experimental and modeling study on adsorption of cationic methylene blue dye onto mesoporous biochars prepared from agrowaste. *Desalination and Water Treatment* 2016; 57(56): 27199-27212.

Bhateria R, Singh R. A review on nanotechnological application of magnetic iron oxides for heavy metal removal. *Journal of Water Process Engineering* 2019; 31: 100845.

Bhatti HN, Hayat J, Iqbal M, Noreen S, Nawaz S. Biocomposite application for the phosphate ions removal in aqueous medium. *Journal of Materials Research and Technology* 2018; 7(3): 300-307.

Bibi I, Nazar N, Ata S, Sultan M, Ali A, Abbas A, Iqbal M. Green synthesis of iron oxide nanoparticles using pomegranate seeds extract and photocatalytic activity evaluation for the degradation of textile dye. *Journal of Materials Research and Technology* 2019; 8(6): 6115-6124.

Ciambelli P, La Guardia G, Vitale L. Nanotechnology for green materials and processes. *In Studies in Surface Science and Catalysis* 2019; 179: 97-116.

Dahlan NA, Ng SL, Pushpamalar J. Adsorption of methylene blue onto powdered activated carbon immobilized in a carboxymethyl sago pulp hydrogel. *Journal of Applied Polymer Science* 2017; 134: 44271.

Fu Y, Xu P, Huang D, Zeng G, Lai C, Qin L, Zhang C. Au nanoparticles decorated on activated coke via a facile preparation for efficient catalytic reduction of nitrophenols and azo dyes. *Applied Surface Science* 2019; 473: 578-588.

Girginova PI, Daniel-da-Silva AL, Lopes CB, Figueira P, Otero M, Amaral VS, Trindade T. Silica coated magnetite particles for magnetic removal of Hg2+ from water. *Journal of colloid and interface science* 2010; 345(2): 234-240.

Hamilton-Amachree A, Iroha NB. Corrosion inhibition of API 5L X80 pipeline steel in acidic environment using aqueous extract of Thevetia peruviana. *Chemistry International* 2020; 6(3): 110-121.

He Y, Wang R, Jiao T, Yan X, Wang M, Zhang L, Peng Q. Facile preparation of self-assembled layered double hydroxide-based composite dye films as new chemical gas sensors. *ACS Sustainable Chemistry & Engineering* 2019; 7(12): 10888-10899.

Hou N, Wang R, Geng R, Wang F, Jiao T, Zhang L, Peng Q. Facile preparation of self-assembled hydrogels constructed from poly-cyclodextrin and poly-adamantane as highly selective adsorbents for wastewater treatment. *Soft Matter* 2019; 15(30): 6097-6106.

Ishtiaq F, Bhatti HN, Khan A, Iqbal M, Kausar A. Polypyrole, polyaniline and sodium alginate biocomposites and adsorption-desorption efficiency for imidacloprid insecticide. *International journal of biological macromolecules* 2020; 147: 217-232. https://doi.org/10.1016/j.ijbiomac.2020.01.022.

Jafarinejad S. Activated sludge combined with powdered activated carbon (PACT process) for the petroleum industry wastewater treatment: a review. *Chemie International* 2017; 3(4): 368.

Jamil A, Bokhari TH, Javed T, Mustafa R, Sajid M, Noreen S, Jilani MI. Photocatalytic degradation of disperse dye Violet-26 using TiO2 and ZnO nanomaterials and process variable optimization. *Journal of Materials Research and Technology* 2020; 9(1): 1119-1128.

Jonidi Jafari A, Rezaei Kalantary R, Babaei AA, Heydari Farsani M, Kakavandi B. Modeling and optimization of adsorption process of reactive dyes on powder activated carbon modified by magnetite nanocrystals. *Journal of Mazandaran University of Medical Sciences* 2016; 26(137): 171-187.

Kakavandi B, Raofi A, Peyghambarzadeh SM, Ramavandi B, Niri MH, Ahmadi M. Efficient adsorption of cobalt on chemical modified activated carbon: characterization, optimization and modeling studies. *Desalination and Water Treatment* 2018; 111: 310-321.

Kakavandi B, Takdastan A, Pourfadakari S, Ahmadmoazzam M, Jorfi S. Heterogeneous catalytic degradation of organic compounds using nanoscale zero-valent iron supported on kaolinite: Mechanism, kinetic and feasibility studies. *Journal of the Taiwan Institute of Chemical Engineers* 2019; 96: 329-340.

Kaur S, Rani S, Mahajan RK, Asif M, Gupta VK. Synthesis and adsorption properties of mesoporous material for the removal of dye safranin: kinetics, equilibrium, and thermodynamics. *Journal of Industrial and Engineering Chemistry* 2015; 22: 19-27.

Kausar A, Iqbal M, Javed A, Aftab K, Bhatti HN, Nouren S. Dyes adsorption using clay and modified clay: a review. *Journal of Molecular Liquids* 2018; 256: 395-407.

Kostyukova D, Chung YH. Synthesis of iron oxide nanoparticles using isobutanol. *Journal of Nanomaterials* 2016. https://doi.org/10.1155/2016/4982675.

Kuang Y, Zhang X, Zhou S. Adsorption of methylene blue in water onto activated carbon by surfactant modification. *Water* 2020; 12(2): 587. https://doi.org/10.3390/w12020587

Minas F, Chandravanshi BS, Leta S. Chemical precipitation method for chromium removal and its recovery from tannery wastewater in Ethiopia. *Chemie International* 2017; 3(4): 291-305.

Mushtaq M, Bhatti HN, Iqbal M, Noreen S. Eriobotrya japonica seed biocomposite efficiency for copper adsorption: isotherms, kinetics, thermodynamic and desorption studies. *Journal of environmental management* 2016; 176: 21-33.

Noreen S, Bhatti HN, Iqbal M, Hussain F, Sarim FM. Chitosan, starch, polyaniline and polypyrrole biocomposite with sugarcane bagasse for the efficient removal of Acid Black dye. *International journal of biological macromolecules* 2020; 147: 439-452. https://doi.org/10.1016/j.ijbiomac.2019.12.257.

Noreen S, Khalid U, Ibrahim SM, Ghani TJA, Iqbal SNM. ZnO, MgO and FeO adsorption efficiencies for direct sky Blue dye: equilibrium, kinetics and thermodynamics studies. *Journal of Materials Research and Technology* 2020; 9(3): 5881-5893.

Qin L, Yi H, Zeng G, Lai C, Huang D, Xu P, Liu X. Hierarchical porous carbon material restricted Au catalyst for highly catalytic reduction of nitroaromatics. *Journal of hazardous materials* 2019; 380: 120864.

Sahoo TR, Prelot B. Adsorption processes for the removal of contaminants from wastewater: the perspective role of nanomaterials and nanotechnology. *In Nanomaterials for the Detection and Removal of Wastewater Pollutants, Elsevier* 2020: 161-222.

Sayhood AA, Mohammed H.J. Synthesis of new azo reagent for determination of Pd (II), Ag (I) and applied to enhance the properties of silver nano particles. *International Journal of Chemical Sciences* 2015; 13(3): 1123-1136.

Shoukat S, Bhatti HN, Iqbal M, Noreen S. Mango stone biocomposite preparation and application for crystal violet adsorption: a mechanistic study. *Microporous and Mesoporous Materials* 2017; 239: 180-189.

Wang C, Yin J, Han S, Jiao T, Bai Z, Zhou J, Peng Q. Preparation of palladium nanoparticles decorated polyethyleneimine/ polycaprolactone composite fibers constructed by electrospinning with highly efficient and recyclable catalytic performances. *Catalysts* 2019; 9(6): 559.

Zhao J, Yin J, Zhong J, Jiao T, Bai Z, Wang S, Peng Q. Facile preparation of a self-assembled artemia cyst shell–TiO2–MoS2 porous composite structure with highly efficient catalytic reduction of nitro compounds for wastewater treatment. *Nanotechnology* 2019; 31(8): 085603.

Zhu J, Wang R, Geng R, Zhang X, Wang F, Jiao T, Peng Q. A facile preparation method for new two-component supramolecular hydrogels and their performances in adsorption, catalysis, and stimuli-response. *RSC advances* 2019; 9(39): 22551-22558.

Pandarakalam JP. The physiology of incarnation process; lessons from pre-birth experiences and reincarnation-type case. *NeuroQuantology* 2019; 17(5): 22-34.